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PHASE FORMATION PROCESSES IN FORMATION OF LOW-MELTING DEVITRIFIED GLAZES

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The phase formation processes are studied for all stages of the synthesis of devitrified glaze coatings for ceramics, which are produced by directed crystallization of β-spodumene, diopside, and gahnite. The mechanism of simultaneous crystallization of a set of prescribed phases is determined, which makes it possible to produce low-melting glass-ceramic glazes with high service parameters under low-temperature fast firing.

The improvement of service characteristics of ceramic materials is traditionally based on using high-quality raw materials and perfecting the ceramic microstructure. However, the quality of ceramic articles can be also improved through deposition of a special vitreous coating, which ensures the required level of aesthetic and technological properties. At present, such coating, as a rule, is implemented in the form of glaze containing inert solid opacifiers, such as zircon, whose resources in Ukraine are extremely limited. In this connection, the prevailing trend until recently consisted in using alternative opacifying ingredients or decreasing the opacifier content in coatings, which deteriorated the service properties of the glazed ceramics.

Reasonable prospects for the development of more functionally perfect ceramics are related to the use of devitrified glazes produced according to glass ceramic technology, involving directed crystallization of glass of the respective chemical composition. The specifics of the directed crystallization method make it possible to produce coatings of wide mineralogical compositions, which makes it possible to vary their properties, depending on the particular service conditions. Furthermore, when used in glaze technology, this method does not require special equipment and can be implemented on available production lines.

A scientifically justified approach to developing compositions of devitrified glazes in theory and in practice is possible only on the basis of the regularities of structure formation in such coatings at all stages of their synthesis. The purpose of the present study was to investigate the phase formation mechanism in devitrified glaze coatings produced under low-temperature fast firing using the method of directed crystallization of a set of prescribed phases: β-spodumene $LiAlSi_2O_6$, gahnite $ZnAl_2O_4$, and diopside $CaMgSi_2O_6$.

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The investigations were performed on coatings whose compositions belong to the system Li_2O – CaO – MgO – ZnO – Al_2O_3 – B_2O_3 – SiO_2 and are limited by the mass contents of the components (%): 3.5, 11.0, 11.0, 6.0, 12.0, 10.0, and 52.5, respectively. The present paper describes the result of studying the phase formation processes in the glaze coating of optimum composition, which maintains such ratio between the phase-forming oxides that in the considered concentration interval preserves the stoichiometry of the synthesized phases [1].

Similarly to glass ceramics [2], the study assumed the existence of a correlation between the processes in the series: batch → melt → glass → crystal for devitrified glaze coatings. Therefore, we primarily investigated the processes occurring at the first stage of the glaze coating synthesis, i.e., the transformation of batch into a melt.

The thermodynamic calculation of Gibbs energy for the reactions proceeding in the batch within the temperature interval 327 – 1327°C demonstrated that the end products of high-temperature reactions between the batch components are gahnite, diopside, and β-spodumene. The heat treatment of the batch in the temperature interval of 600 – 1100°C and a subsequent x-ray phase analysis of the sintered cake corroborated the formation of the specified compounds predicted by the thermodynamic calculations and made it possible to identify the sequence of phase transformations occurring in the batch heating (Fig. 1). It can be seen that the transformations follow the following scheme: willemite + gahnite + diopside + quartz-type solid solutions (600 – 900°C) → gahnite + diopside + β-spodumene solid solutions (1000 – 1100°C). A further increase in the temperature leads to the dissolution of the formed compounds in the melt. According to x-ray phase analysis, the frit obtained at 1350°C is x-ray-amorphous.

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At the same time, the spectral analysis of the frit revealed the presence of groups with chemical bonds corresponding to future crystalline phases. This is corroborated by comparative analysis of the IR spectra of the frit and the glass ceramic coating: the transition from the vitreous state to the crystallized state is accompanied by an increase in the intensity of the absorption bands typical of the silicon-oxygen complexes of diopside, β-spodumene, and gahnite (Fig. 2). Thus, the absorption band with the maximum at 740 cm^{-1} points to the presence of the Si–O–Al bond, which is the main structural group of β-spodumene solid solution [3]. The maximum at the frequency 1025 cm^{-1} belongs to the same compound. The narrowing of the absorption bands and their heightened intensity in the frequency interval 400 – 500 cm^{-1}, as well as the maximum at 950 cm^{-1}, is evidence of diopside formation. Gahnite is the compound responsible for the formation of a maximum at frequencies of 640 and 660 cm^{-1} [4].

The studies of the frit by the direct electron microscopy method corroborated the results of the spectral analysis, which registered liquation with a drop size up to 1 μm in the frit. Employing x-ray microanalysis, it was established that the vitreous phase of the drops has nonuniform concentrations of aluminum, zinc, lithium, and calcium ions, and to a lesser extent, magnesium ions, whereas the matrix is mainly the magnesium-boron-silicon phase. Analysis of the obtained results suggests that the vitreous phase isolated in drops has predominantly a more ordered structure than the surrounding glass, and the composition of the liquation inhomogeneities approximates the composition of crystalline compounds which under favorable conditions can be released from this glass (diopside, β-spodumene, gahnite).

The modifications occurring in the phase composition of the coating during its transition from the vitreous state to the crystallized state were investigated, employing high-temperature x-ray analysis. The samples under consideration were crystallized for 6 min at 750°C. The studies were carried out by gradual heating of the samples up to 750°C, holding them at the specified temperature, and a subsequent temperature rise to 850°C. A segment of the diffraction pattern within the limits of the double angles of reflection from 22 to 42° selected for the analysis contained the reference reflections of β-spodumene solid solution (d = 0.348 nm), gahnite (d = 0.244 nm), and diopside (d = 0.299 nm).

As can be seen in Fig. 3, the main primary phases of the resulting coating are β-spodumene solid solution, diopside, and gahnite. It should be noted that the registered decrease in the temperatures at which the compounds are crystallized under firing, compared to the temperatures of their intense formation in the batch, points to a decreased energy barrier in the formation of the specified phases. This is due to the fact that the glaze melt and, consequently, the frit contain microinhomogeneities, which pre-

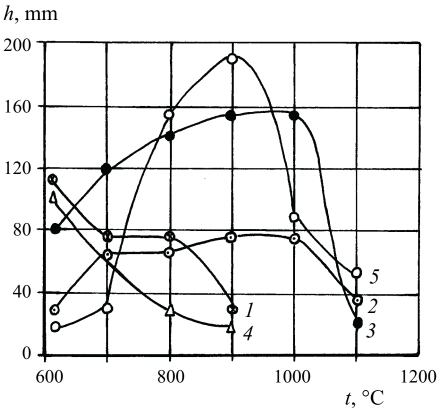

Fig. 1. Qualitative characteristics of reactions between the batch components in heating, based on the intensity variation of the characteristic peaks on x-ray patterns: *1*) willemite (d = 0.263 nm); *2*) gahnite (d = 0.244 nm); *3*) diopside (d = 0.299 nm); *4*) β-eucryptite solid solution of quartz-O type (d = 0.454 nm); *5*) β-spodumene solid solution of quartz-K type (d = 0.385 nm).

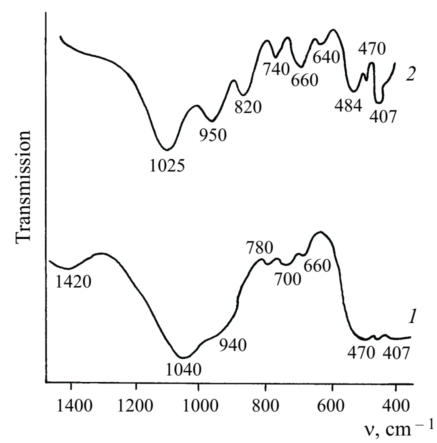

Fig. 2. IR transmission spectra of frit (*1*) and glass ceramic coating obtained at 750°C (*2*).

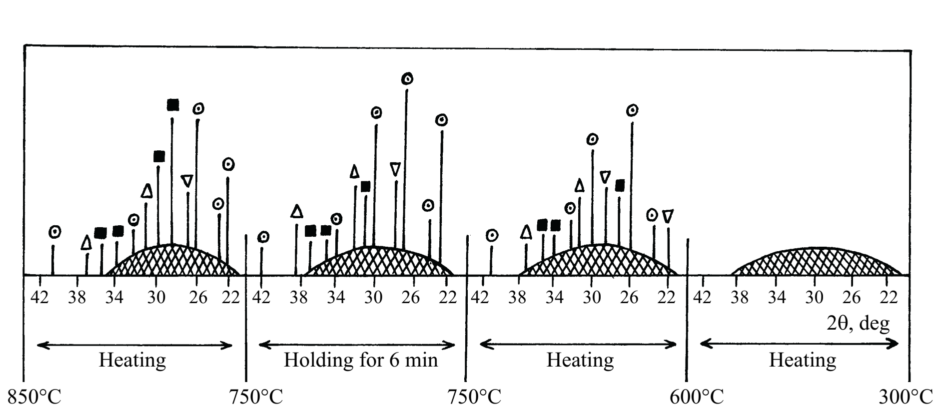

Fig. 3. Thermo-x-ray patterns of the glaze coatings: ⊙) β-spodumene solid solution; △) gahnite; ■) diopside; ▽) β-cristoballite.

serve the near order and structural specifics of the respective compounds, thus contributing to the high rate of the formation of crystal centers of these phases in firing of the coating. This is corroborated by the data of high-temperature x-ray phase analysis.

Studies of the phase formation processes at all stages of the synthesis of low-melting glass ceramic glazes made it possible to identify the mechanism of the structure formation in coatings of this type. The mechanism on the whole can be reduced to the following. In fritting, the end products of the reactions taking place in batch heating become melted, whereas the glaze melt preserves the silicon-oxygen complexes corresponding to the future crystalline phases. The latter develop microinhomogeneities in the frit, which preserve the near order and the structural specifics of the future crystals.

Under repeated heat treatment, the nucleation complexes contained in the drops diffuse into the matrix glass and give origin to the formation of precisely those compounds that were the end products of the reactions in the batch. As was shown by electron microscopy and petrography data, crystallization in this case occurs both at the grain borders and directly from the melt. The high rate of formation of the crystallization centers caused by the presence in the initial glaze glass of structural ordering groups, which are near in composition to the composition of the respective crystalline phases, as well as the low growth rate of new formations, determined by the increase in the melt viscosity under crystallization, leads to the formation of the fine-crystalline structure of the glaze coating. The petrography and electron microscopic studies established that the size of single crystals formed in the coatings under fast firing at 750°C is less than 5 μm, and the size of crystalline aggregates is 7 – 10 μm.

Taking into account the established relationship between the processes of glaze glass production and its subsequent crystallization, glass ceramic glazes with the formation temperature 750 – 850°C were synthesized for the purpose of coatings for ceramics produced under fast secondary firing (30 – 45 min) and having a TCLE of the ceramic substrate of $(40 - 70) \times 10^{-7}\ K^{-1}$. The glaze coatings have a dull white surface, a high degree of opacification (although traditional opacifiers are absent from their compositions), and a thermal coefficient of expansion which can be controlled by varying the temperature and duration of firing within the specified limits, as well as high parameters of heat resistance (400°C) and microhardness (8700 MPa) and high chemical resistance to water, 20% solutions of HCl and H_2SO_4, and 2 N solution of NaOH (99%),

The developed glaze can be used in the production of certain types of building ceramics, household articles, and majolica, as well as in the development of integrated protection for ceramic products and structures intended for operation in difficult conditions.

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